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Photochemical Syntheses of Apogalanthamine Analogs as α-Adrenergic Blocking Agents[1]

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The apogalanthamine analogs, 10,11-methylenedioxy- and 10,11-dimethoxy-5,6,7,8-tetrahydrodibenz[*c*,*e*]azocines (**1** and **2**, respectively) as α-adrenergic blocking agents were synthesized by photolysis of N-benzyl-2-iodo-4,5-methylenedioxy- and N-benzyl-2-iodo-4,5-dimethoxy-β-phenethylamine (**20** and **21**, respectively). 2,3-Methylenedioxy-, and 2,3-dimethoxy-5,6,7,8-tetrahydrodibenz[*c*,*e*]azocine (**9** and **10**, respectively) were obtained similarly from N-(2-iodo-4,5-methylenedioxybenzyl)- and N-(4,5-dimethoxy-2-iodobenzyl)-β-phenethylamine (**18** and **19**, respectively). The yields of **9** and **10** from the iodo-amines (**18** and **19**) having an iodine atom in the benzyl group were found to be better than those of **1** and **2** from iodides **20** and **21** respectively having a halogen atom in the phenethyl group.

Keywords——apogalanthamine analog; α-adrenergic blocking agent; tetrahydrodibenz[*c*,*e*]azocine; photochemical synthesis; N-benzyl-β-phenethylamine; iodination; photolysis

In the previous paper we reported the chemical syntheses[3] of the apogalanthamine analogs, 10,11-methylenedioxy-, 10,11-dimethoxy-, and 11,12-dimethoxy-5,6,7,8-tetrahydrodibenz[*c*,*e*]azocine (**1**, **2**, and **3**, respectively), and their N-substituted derivatives (**4**, **5**, **6**, **7**, and **8**), having α-adrenergic blocking activities on rat aorta strips,[4,5] and the syntheses[3] of the related compounds, 2,3-methylenedioxy-, 2,3-dimethoxy-, and 11-methoxy-5,6,7,8-tetrahydrodibenz[*c*,*e*]azocine (**9**, **10**, and **11**, respectively).

This paper reports the photochemical syntheses of apogalanthamine analogs **1** and **2** having pharmacological activities and of the related compounds **9** and **10**.

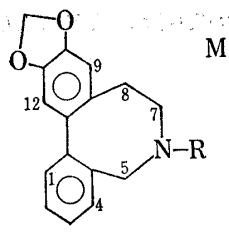
Recently, Jeffs, *et al.*[6] synthesized dibenzazocines (**12**—**14**) by photolysis of the corresponding N-(2-halogenobenzyl)-β-phenethylamines (**15**—**17**) which had a halogen atom in the benzyl group. This paper described photolysis of similar iodo-amines, such as N-(2-iodo-4,5-methylenedioxybenzyl)- and N-(2-iodo-4,5-dimethoxybenzyl)-β-phenethylamine (**18** and **19**, respectively) and of other iodo-amines having an iodine atom in the phenethyl group, such as N-benzyl-2-iodo-4,5-methylenedioxy- and N-benzyl-2-iodo-4,5-dimethoxy-β-phenethylamine (**20** and **21**, respectively).

Syntheses of N-Benzyl-β-phenethylamine Derivatives (18—21 and 35)

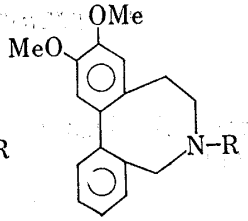
Compounds **18** and **19** were prepared by sodium borohydride (SBH) reduction of the Schiff's bases of β-phenethylamine (**22**) with 6-iodopiperonal (**23**) and 6-iodoveratraldehyde (**24**), respectively, as shown in Table I.

Compounds **20** and **21** were obtained similarly by SBH reduction of the Schiff's bases of benzaldehyde (**25**) with 2-iodo-4,5-methylenedioxy- and 4,5-dimethoxy-2-iodo-β-phenethyl-

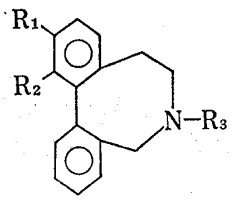
1) This forms Part XVII of "Studies on the Syntheses of Benzoheterocyclic Compounds" by S. Kobayashi, Part XVI: ref. 3.
2) Location: *1-78, Sho-machi, Tokushima, 770, Japan.*
3) S. Kobayashi, M. Kihara, S. Shizu, S. Katayama, H. Ikeda, K. Kitahiro, and H. Matsumoto, *Chem. Pharm. Bull.* (Tokyo), **25**, 3312 (1977).
4) Y. Ishida, K. Watanabe, S. Kobayashi, and M. Kihara, *Jpn. J. Pharmacol.* **26**, 607 (1976).
5) Y. Ishida, K. Watanabe, S. Kobayashi, and M. Kihara, *Chem. Pharm. Bull.* (Tokyo), **25** 1851 (1977).
6) P.W. Jeffs, J.F. Hansen, and G.A. Brine, *J. Org. Chem.*, **40**, 2883 (1975).



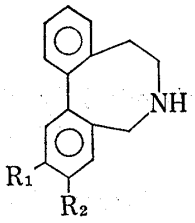
1: R=H
4: R=Me
5: R=Et
6: R=CH_2CH_2Br



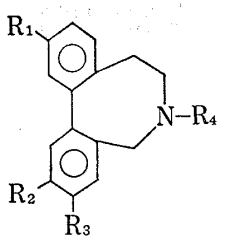
2: R=H
7: R=Me



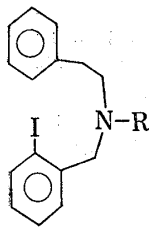
3: $R_1=R_2=OMe$, $R_3=H$
8: $R_1=R_2=OMe$, $R_3=Me$
11: $R_1=OMe$, $R_2=R_3=H$



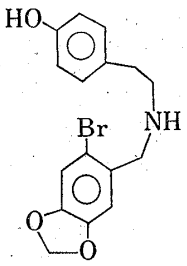
9: R_1, $R_2=OCH_2O$
10: $R_1=R_2=OMe$



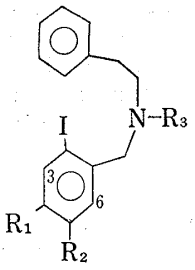
12: $R_1=R_2=R_3=R_4=H$
13: $R_1=R_2=R_3=H$, $R_4=Me$
14: $R_1=OH$, R_2, $R_3=OCH_2O$, $R_4=H$



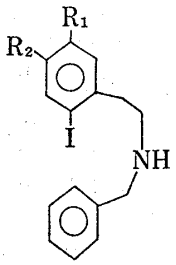
15: R=H
16: R=Me



17



18: R_1, $R_2=OCH_2O$, $R_3=H$
19: $R_1=R_2=OMe$, $R_3=H$
33: R_1, $R_2=OCH_2O$, $R_3=Ac$



20: R_1, $R_2=OCH_2O$
21: $R_1=R_2=OMe$

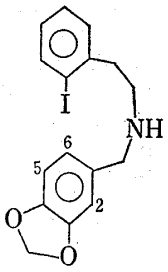


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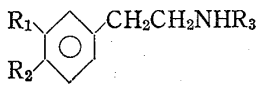
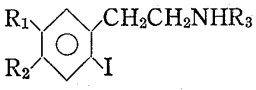
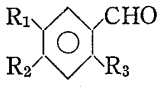
Chart 1



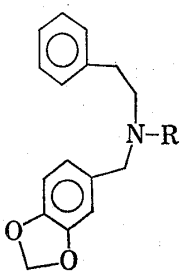
22: $R_1=R_2=R_3=H$
28: R_1, $R_2=OCH_2O$, $R_3=H$
29: R_1, $R_2=OCH_2O$, $R_3=Ac$
32: $R_1=R_2=OMe$, $R_3=Ac$
41: $R_1=R_2=OMe$, $R_3=H$



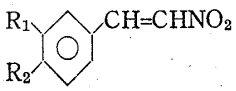
26: R_1, $R_2=OCH_2O$, $R_3=H$
27: $R_1=R_2=OMe$, $R_3=H$
30: R_1, $R_2=OCH_2O$, $R_3=Ac$
31: $R_1=R_3=OMe$, $R_3=Ac$
36: $R_1=R_2=R_3=H$



23: R_1, $R_2=OCH_2O$, $R_3=I$
24: $R_1=R_2=OMe$, $R_3=I$
25: $R_1=R_2=R_3=H$
37: R_1, $R_2=OCH_2O$, $R_3=H$
39: $R_1=R_2=OMe$, $R_3=H$



34: R=Ac
42: R=H



38: R_1, $R_2=OCH_2O$
40: $R_1=R_2=OMe$

Chart 2

amine (**26** and **27**, respectively). Kallianpur and Merchant[7] prepared 2-iodo-4,5-methylenedioxytoluene by iodination of 3,4-methylenedioxytoluene in ethanol with iodine in the presence

7) C.S. Kallianpur and J.R. Merchant, *J. Indian Chem. Soc.*, **38**, 27 (1961).

Table I. Syntheses of N-Benzyl-β-phenetyhlamine Derivatives (**18**—**21** and **35**)

Formation of Schiff's base[a]			Reduction[b]			
Aldehyde (g)	Amine (mg)	Reaction time (hr)	$NaBH_4$ (mg)	EtOH:$CHCl_3$ (3:2)(ml)	Reaction time (hr)	Product as hydrochloride mg(%)[c]
23[d] (0.30)	**22** (125)	3.5	43	5	7.5	**18** 157(36.4)
24[e] (0.50)	**22** (200)	4.5	66	8	10.5	**19** 602(84.1)
25 (4.20)	**26** (761)	10.5	1670	60	19	**20** 846(77.5)
25 (3.15)	**27** (524)	9	853	40	8	**21** 304(41.1)
37 (0.15)	**36** (200)	4	45	5	5.5	**35** 242(71.6)

a) Reaction at 110°.
b) Reaction at room temperature.
c) Yield from the amine.
d) S. Kobayashi, M. Kihara, T. Hashimoto, and T. Shingu, *Chem. Pharm. Bull.* (Tokyo), **24**, 716 (1976).
e) A. Rilliet, *Helv. Chim. Acta*, **5**, 547 (1922).

Table II. Iodination of N-Acetyl-β-phenethylamine Derivatives[a] (**29**, **32**, and **34**)

Starting material (mg)	I_2 (g)	HgO (g)	DMSO (ml)	Reaction time (hr)	Product mg (%)
29 59	0.368	0.295	7	9	**30** 77(81.2)
32 404	2.266	1.851	10	6	**31** 433(68.5)
34 796	3.400	2.900	10	25	**33** 463(40.9)

a) Reaction at room temperature.

of mercuric oxide. However, attempts to iodinate 3,4-methylenedioxy-β-phenethylamine (**28**) and its amide (**29**) by this method were unsuccessful. However, the amide (**29**) was found to give the iodide (**30**) in 81.2% yield when dimethyl sulfoxide (DMSO) was used instead of ethanol as solvent in the reaction (see Table II). The iodide (**31**) was similarly obtained in 68.5% yield from the amide (**32**). The hydrolyses of **30** and **31** with methanolic hydrochloric acid gave **26** and **27**, respectively.

By this iodination method the amide (**33**) was also obtained in 40.9% yield from the

Table III. NMR Spectra of the Free Bases of N-Benzyl-β-phenethylamine Derivatives (**18**—**21** and **35**)

Compd.	Aromatic H				OCH_3 or OCH_2O				$ArCH_2N$-	$ArCH_2CH_2N$	NH
	In phenethyl group		In benzyl group		In phenethyl group		In benzyl group				
	C-3	C-6	C-3	C-6	C-4	C-5	C-4	C-5			
18				6.86(s)			5.91 (s)		3.72 (m)	2.86 (m)	1.72 (m)
19			7.17 (s)	6.87 (s)			3.83 (s)	3.83 (s)	3.74 (m)	2.87 (m)	1.89 (s)
20	7.17 (s)	6.18 (s)			5.89 (s)				3.89 (m)	2.84 (m)	1.58 (s)
21		6.73(s)			3.84 (s)	3.84 (s)			3.84 (m)	2.90 (m)	2.12 (s)
35[a]			6.71 (d, J= 3 Hz) (C-2)	6.75 (d, J= 8 Hz) (C-5)			5.88 (s) (C-3 and C-4)		3.72 (m)	2.88 (m)	1.52 (s)

a) The numbering of this compound is different from those of the other compounds.

amide (**34**) (see Table II). Hydrolysis of **33** similarly gave **18**.

Compound **35** was also prepared from 2-iodo-β-phenethylamine (**36**) and piperonal (**37**) as shown in Table I.

The structures of these amines (**18**—**21** and **35**) were established by the nuclear magnetic resonance (NMR) spectral data on their free bases and by elementary analysis of their hydrochlorides (see Tables III and IV).

Table IV. Hydrochlorides of N-Benzyl-β-phenethylamine Derivatives (**18**—**21** and **35**)

Hydrochloride	Appearance (Recrystn. solvent)	mp (°C)	Formula	Analysis (%) Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
18	Needles (Methanol)	209—213	$C_{16}H_{16}INO_2 \cdot HCl$	46.01	4.10	3.35	45.83	4.04	3.06
19	Needles (Methanol)	214—217	$C_{17}H_{20}INO_2 \cdot HCl$	47.07	4.88	3.23	47.06	4.91	3.23
20	Needles (Acetone)	105—108	$C_{16}H_{16}INO_2 \cdot HCl \cdot 1/2H_2O$	45.03	4.25	3.28	44.77	4.51	3.08
21	Cubes (Acetone)	173—175	$C_{17}H_{20}INO_2 \cdot HCl$	47.07	4.88	3.23	47.20	5.08	2.93
35	Cubes (Acetone–methanol)	178—180	$C_{16}H_{16}INO_2 \cdot HCl$	46.01	4.10	3.35	46.02	4.14	3.12

Photochemical Cyclization of N-Benzyl-β-phenethylamine Derivatives (**18**—**21**)

Irradiation of the hydrochloride of **19** in aqueous solution gave the cyclization product (**10**) (20.7% yield) as an oil. The NMR spectrum of the cyclization product (**10**) showed the C-5 methylene proton signals (δ 3.86 and 3.10) as a pair of AB-type doublets, which are the characteristic signals[3] of these dibenzazocines (see Table V). Furthermore, the oily material (**10**) was crystallized as its neutral styphnate, mp 221—224° (dec.), which was found to be identical with an authentic sample[3] of the styphnate by direct comparison.

The other dibenzazocines **1**, **2**, and **9** were obtained similarly by photochemical cyclization of **20**, **21**, and **18**, respectively, as shown in Table VI and were identified by direct comparison with authentic samples[3] of these dibenzazocines.

From these results, the yields of dibenzazocines **9** and **10** from the iodides (**18** and **19**, respectively) having an iodine atom in the benzyl group were found to be better than those of dibenzazocines **1** and **2** from the iodides (**20** and **21**, respectively) having an iodine atom

Table V. Chemical Shifts[a] of the free Bases of Dibenzazocines (**1**,**2**,**9**, and **10**) (in $CDCl_3$, δ)

Compd.	Aromatic H C-1	Aromatic H C-4	Aromatic H C-9	Aromatic H C-12	C-5 H_2[b]	OCH_2O or OCH_3 C-2	OCH_2O or OCH_3 C-3	OCH_2O or OCH_3 C-10	OCH_2O or OCH_3 C-11	NH
1			6.69	6.75	3.92(d) 3.21(d)			5.98		1.88
2			6.75	6.80	3.97(d) 3.25(d)			3.96	3.90	1.27
9	6.76	6.79			3.77(d) 3.04(d)	5.95				1.80
10	6.81	6.83			3.86(d) 3.10(d)	3.87	3.92			1.98

a) Signals are for singlets except for those combined with parentheses.
b) Signals are for AB-type doublets having a coupling constant of 14 Hz.

Table VI. Photolysis of Hydrochlorides of N-Benzyl-β-phenethylamine Derivatives (**18**—**21**)

Hydrochloride of, (mg)	H_2O (ml)	Reaction time (hr)	Dibenzazocine mg (%)	mp (°C)	Formula	Analysis (%)[a] Calcd. (Found) C	H	N
18 (1056)	210	433	**9** 53.0 (Oil) (8.3) 52.1 (Styphnate)[b] (5.5)	220—222 (dec.)	$C_{16}H_{15}NO_2 \cdot 1/2C_6H_3N_3O_8$	60.71 (60.38)	4.43 (4.39)	9.32 (9.05)
19 (327)	60	551	**10** 42.0 (Oil) (20.7) 39.0 (Styphnate)[b] (13.2)	221—224 (dec.)	$C_{17}H_{19}NO_2 \cdot 1/2C_6H_3N_3O_8 \cdot 1/2H_2O$	59.92 (60.28)	5.41 (5.20)	8.74 (8.68)
20 (543)	110	217	**1** 5.8 (Oil) (1.8) 2.6 (Cubes) (0.8)	95—98	$C_{16}H_{15}NO_2$	75.87 (75.57)	5.97 (5.88)	5.53 (5.30)
21 (252)	50	180	**2** 5.1 (Oil) (3.3) 3.3 (Cubes) (2.1)	117—121	$C_{17}H_{19}NO_2$	75.81 (75.52)	7.11 (7.16)	5.20 (4.97)

a) For crystalline dibenzazocines or crystalline styphnates.
b) This is a neutral styphnate.

in the phenethyl group. Consistent with this, an attempt to cyclize N-(3,4-methylenedioxybenzyl)-2-iodo-β-phenethylamine (**35**) by irradiation was unsuccessful.

Experimental

All melting points are given as uncorrected values. The spectrophotometers used were a Hitachi EPI-G2 model for infrared (IR) spectra, and a JEOL JNM-PS-100 model for NMR spectra using TMS as an internal standard. The abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Irradiation was carried out with a RIKO UVL-400H lamp placed 20 cm from the solution.

N-Acetyl-3,4-methylenedioxy-β-phenethylamine (**29**)——A mixture of **37** (12 g) and *n*-butylamine (23 g) was heated at 107° for 2 hr. The reaction mixture was concentrated to a residue, which was mixed with AcOH (12 ml) and CH_3NO_2 (9 ml). The mixture was stirred at room temperature for 4 hr to give yellow needles (15 g, 97.3%) of 3,4-methylenedioxy-(2-nitrovinyl)benzene (**38**), mp 156—157° (from ether) (lit.[8] mp 159°). *Anal.* Calcd. for $C_9H_7NO_4$: C, 55.95; H, 3.65; N, 7.25. Found: C, 55.89; H, 3.58; N, 7.36.

A solution of **38** (6.0 g) in tetrahydrofuran (THF) (140 ml) was slowly added to a suspension of $LiAlH_4$ (7.2 g) in THF (90 ml) at room temperature over a period of 40 min and then stirred for 3.5 hr. Working up in the usual way gave **28** (3.57 g, 69.0%) as an oil, which was crystallized as its hydrochloride, mp 204—206° (dec.). *Anal.* Calcd. for $C_9H_{11}NO_2 \cdot HCl$: C, 53.60; H, 5.99; N, 6.95. Found: C, 53.85; H, 6.10; N, 6.92.

Acetic anhydride (25 ml) and **28** (3.57 g) were heated at 60° for 1 hr. Concentration of the solution gave a solid, which was recrystallized from benzene as white needles (2.61 g, 58.2%) of **29**, mp 100—101° (lit.[9] mp 108—109°). *Anal.* Calcd. for $C_{11}H_{13}NO_3$: C, 63.75; H, 6.32; N, 6.76. Found: C, 63.70; H, 6.32; N, 6.65. IR ν_{max}^{KBr} cm^{-1}: 1620 (C=O). NMR ($CDCl_3$–D_2O) δ: 6.66 (3H, m, aromatic H), 5.93 (2H, s, OCH_2O), 5.64 (1H, br s, NHCO), 3.47 (2H, t, J=7 Hz, $ArCH_2C\underline{H}_2N$), 2.75 (2H, t, J=7 Hz, $ArC\underline{H}_2CH_2N$), 1.96 (3H, s, CH_3CO).

N-Acetyl-3,4-dimethoxy-β-phenethylamine (**32**)——The amide (**32**) was prepared in the same manner as **29**: veratraldehyde (**39**) (5.02 g), *n*-butylamine (20.5 ml), AcOH (7.5 ml), and CH_3NO_2 (4.0 ml) were treated to give 3,4-dimethoxy(2-nitrovinyl)benzene (**40**) (5.82 g, 92.1%), mp 138—140° (from benzene) (lit.[10] mp 140°). *Anal.* Calcd. for $C_{10}H_{11}NO_4$: C, 57.41; H, 5.30; N, 6.70. Found: C, 57.55; H, 5.26; N, 6.69.

Reduction of **40** (3.59 g) in THF (90 ml) with $LiAlH_4$ (5.2 g) in THF (30 ml) gave 3,4-dimethoxy-β-phenethylamine (**41**), (2.41 g, 77.6%) as an oil. Acetylation of **41** (2.41 g) with acetic anhydride (18 ml) gave **32** (1.72 g, 57.8%) as white cubes, mp 95—97° (from benzene) [lit. bp 213° (4 mmHg)].[11] *Anal.* Calcd. for $C_{12}H_{17}NO_3$: C, 64.55; H, 7.68; N, 6.27. Found: C, 64.32; H, 7.48; N, 6.04. IR ν_{max}^{KBr} cm^{-1}: 1630 (C=O).

N-Acetyl-4,5-dimethoxy-2-iodo-β-phenethylamine (**31**)——To a solution of **32** (404 mg) in DMSO (10 ml) were added iodine (2.266 g) and HgO (yellow) (1.851 g). The mixture was stirred at room temperature for 6 hr, mixed with H_2O (30 ml), and then filtered. The filtrate was extracted with $CHCl_3$, and the extract was washed successively with 10% KOH, 10% $Na_2S_2O_3$, and then H_2O. Evaporation of the solvent gave

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Table VII. Iodophenethylamine Derivatives (**30**, **31**, and **33**)

Compd.	mp[a] (°C)	Formula	Analysis (%) Calcd. (Found) C	H	N	IR ν_{max}^{KBr} cm^{-1} (C=O)	NMR ($CDCl_3$, δ) Aromatic H	OCH_3 or OCH_2O	CH_3CO
30	158—160	$C_{11}H_{12}INO_3$	39.62 (39.66)	3.49 (3.63)	4.07 (4.20)	1640	7.23 (1H, s, C-3) 6.75 (1H, s, C-6)	5.96 (2H, s)	2.00 (3H, s)
31	110—111	$C_{12}H_{16}INO_3$	41.27 (41.03)	4.62 (4.49)	4.01 (3.72)	1630	7.20 (1H, s, C-3) 6.75 (1H, s, C-6)	3.84 (6H, s)	1.96 (3H, s)
33	107—109	$C_{18}H_{18}INO_3$	51.08 (50.85)	4.29 (4.28)	3.31 (3.18)	1635	6.76 and 6.56 (2/3 and 1/3 H, respectively, each s, C-6)	5.96 and 5.94[b]	2.08 and 2.04 (2H and 1H, respectively, each s)

a) All these compounds were recrystallized from benzene.
b) These singlets have 2H in total.

31 (433 mg, 68.4%) as white cubes, mp 110—111° (from benzene).

Iodination of **29** and **34** was carried out similarly, as shown in Table II. Physical and spectral data on the products (**30**, **31**, and **33**) are summarized in Table VII.

N-Benzyl-4,5-dimethoxy-2-iodo-β-phenethylamine (21)——The amide (**31**) (630 mg), 20% HCl (20 ml), and MeOH (20 ml) were refluxed for 17 hr. The solvent was evaporated off and the residue was made alkaline with 10% NaOH. The aqueous solution was extracted with ether. The extract was washed with H_2O, dried, and concentrated to give 524 mg (94.5%) of **27** as an oil. The amine (**27**) (524 mg) and **25** (3.15 g) were heated in a sealed tube at 110° for 9 hr. Concentration of the mixture gave a residue, which was dissolved in EtOH–$CHCl_3$ (3 : 2) (40 ml). To the solution $NaBH_4$ (853 mg) was added slowly over a period of 40 min at room temperature and the mixture was stirred for 8 hr. Working up in the usual way gave **21** (420 mg) as an oil, which was converted to its hydrochloride (304 mg, 41.1%), mp 160—169° by addition of conc. HCl in acetone. Recrystallization of the crude material from acetone gave white cubes, mp 173—175°.

The other amines **18**—**20** and **35** were prepared similarly, as shown in Table I. Their physical and spectral data are summarized in Tables III and IV.

Hydrolysis of amide **30** (630 mg) with 20% HCl (17 ml)–MeOH (17 ml) gave the free base (477 mg, 86.6%) of **26** in a similar reaction to that for **27**.

N-Acetyl-N-(3,4-methylenedioxybenzyl)-β-phenethylamine (34)——The hydrochloride [4.03 g, mp 230—233° (dec.)] of the amine (**42**) was prepared in 87.4% yield from **22** (2.23 g) and **37** (3.32 g) in a similar manner to **21**. *Anal.* Calcd. for $C_{16}H_{17}NO_2 \cdot HCl$: C, 65.86; H, 6.22; N, 4.80. Found: C, 65.71; H, 6.20; N, 4.78. Acetylation of **42** [prepared from its hydrochloride (1.50 g)] with acetic anhydride (6 ml) at 60° gave **34** (1.44 g) as an oil, which was iodinated, as shown in Table II.

Photolysis of the Hydrochloride of N-(2-Iodo-4,5-methylenedioxybenzyl)-β-phenethylamine (18)——A solution of the hydrochloride (1.056 g) of **18** in H_2O (210 ml) was irradiated under N_2 with stirring at room temperature for 433 hr. The reaction mixture was filtered and the filtrate was made alkaline (pH 10.5) with Na_2CO_3 and extracted with ether. The red-brown oil (302 mg) obtained from the extract was submitted to preparative thin-layer chromatography (TLC) using Al_2O_3-[benzene-acetone (4 : 1)]. Elution of material of *Rf* 0.04—0.35 with $CHCl_3$–MeOH–acetone (1 : 1 : 1) gave 53 mg (8.3%) of the cyclization product (**9**) as a pale brown oil. The NMR spectrum of this material was identical with that of an authentic sample[3] of **9**. This oily product (**9**), was crystallized as its neutral styphnate (see Table VI).

Photolysis of the hydrochlorides of **19**, **20**, and **21** were carried out similarly as shown in Table VI, and the products (**1**, **2**, **9**, and **10**) were found to be identical with the corresponding authentic samples[3] by direct comparison.

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